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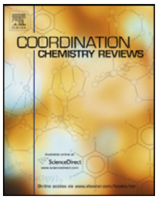

Review

Synthesis, structure and reactivity of complexes containing a transition metal–bismuth bond

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ABSTRACT

The transition metal chemistry of bismuth has attracted significant interest since the 1970s. The low cost and high abundance of bismuth(III) reagents, such as the trihalides, makes them ideal starting materials and the size of the bismuth centre allows three- and higher-coordinate complexes to be synthesised, in which the bismuth atom is linked to one or more transition metal fragments. The ability to vary these metal fragments gives access to a plethora of available structures, with cyclopentadienylcarbonyl, metal carbonyl and sandwich compounds of bismuth in existence. Significant recent study has focused on applications in catalysis, where bismuth species can act as cross-coupling agents in carbon–carbon, carbon–nitrogen and carbon–oxygen bond forming reactions. Another striking feature is the variation in bonding situations that can be observed when studying the organometallic chemistry of bismuth. For example, dative and covalent interactions have been reported, in addition to cases of dibismuth acting as a two-, four- or six-electron donating ligand. This review aims to demonstrate the multi-faceted nature of the transition metal chemistry of bismuth and provide a detailed coverage of this topic.

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1. Introduction

As one of the heaviest elements in the periodic table, bismuth has attracted significant interest resulting in a rich chemistry and a wide array of organometallic complexes. More generally, great progress has been made in the organometallic chemistry of all the group 15 elements [1–4], with many analogous complexes and similar properties in evidence for arsenic, antimony and bismuth [5]. The low cost and high abundance of bismuth(III) reagents, such as the trihalides, makes them ideal starting materials for the synthesis of transition metal–main group complexes. The size of the bismuth centre allows three- and higher-coordinate complexes to be synthesised, in which the bismuth atom is linked to one or more transition metal fragments [6]. The ability to vary these metal fragments gives access to a plethora of available structures, with cyclopentadienylcarbonyl [7], metal carbonyl and sandwich compounds of bismuth in existence [8].

The coordination chemistry of both antimony and bismuth is dominated by the Lewis acidic nature of the main-group centre, often resulting in oligomeric structures in solution and in the solid state [9]. This Lewis acidity is surprising, considering the presence of a lone pair of electrons centred on the main group atom, which results in Lewis basicity for phosphines and arsines. In the case of trivalent bismuth halides, the observed Lewis acidity is caused by relativistic contraction of the valence Bi 6s orbital, which reduces its ability to mix with the halide σ-orbitals [10]. The trihalides and phenyl bismuth dihalides form a range of coordination compounds with ligands such as phosphines or halide ions; for example, $BiPhX_2$ crystallises from tetrahydrofuran (THF) as the polymeric species $[BiPhX_2(THF)]$ displaying intermolecular halide bridges [11]. Such structures can be rationalised by adopting the bonding model proposed by Norman, whereby the Bi–X or Sb–X σ*-orbitals are the acceptor orbitals rather than the conventional view using vacant d-orbitals. The crystal structures of such compounds reveal identifiable primary and secondary E–X interactions (E = Sb, Bi) [12], the difference between which decreases as the halide is varied from chloride to iodide. In a two-orbital system, the antibonding σ*-orbital is polarised towards the less electronegative main-group element, and can act as a Lewis acidic site centred on E through which a ligand can bind [9]. As electronegativity decreases as the group is descended, these secondary interactions are more pronounced for bismuth compounds than the corresponding antimony analogues. A well known, and characterised, example of such an oligomeric structure in a transition metal–bismuth compound is the planar, six-membered ring formed by trimerisation in the solid state of $[\{Cp(CO)_2Fe\}_2BiCl]$ ($Cp = \eta^5\text{-}C_5H_5$) (**2**) [13,14], as shown in Fig. 1.

Significant recent study has focussed on applications in catalysis, where bismuth species can act as cross-coupling agents in carbon–carbon [15–26], carbon–nitrogen [27] and carbon–oxygen [28] bond forming reactions. The low toxicity and ease of handling of arylbismuth compounds makes them comparable with organoboronic acids used in Suzuki–Miyaura type reactions, however, the ability of triarylbismuth compounds to deliver three aryl groups per molecule allows atom-efficient reactions to be developed [29]. The drive for environmentally friendly industrial processes has focussed research into these compounds, with significant contributions from the groups of Shimada, Tanaka and Rao. Tanaka and co-workers reported the cross-coupling between a series of organobismuth dialkoxides, bearing phenyl- and methyl-as the transferrable groups, with aryl and vinyl triflates [16,17]. The reactions were undertaken at room temperature, with high yields obtained when aryl and vinyl triflates with electron-withdrawing substituents were used as the substrate. Two catalytic cycles were proposed, the first requires the oxidative addition of the C–Bi bond to the palladium centre, the product of which then undergoes a metathesis reaction with the triflate. The second mechanism begins with oxidative addition of the triflate, followed by transmetalation and reductive elimination to give the cross-coupling product (Fig. 2). In a later paper, Rao et al. concluded that the latter was the more likely following further mechanistic studies.

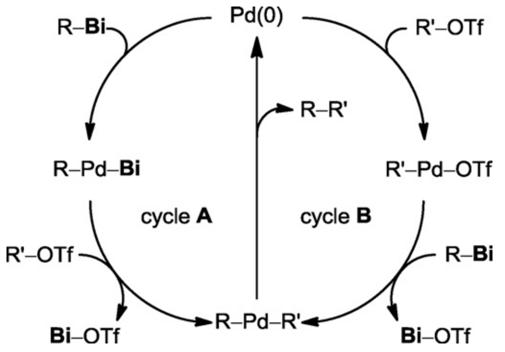


Fig. 2. Proposed catalytic cycles ($Bi = BiR_2$).

Such reactions are not limited to palladium(0) catalysts, examples of palladium(II) [19], rhodium(I) [30] and copper [27] catalysts displaying activity with bismuth reagents can be found in the literature. Venkatraman and Li reported conjugated addition reactions, in the presence of a rhodium(I) catalyst, between α,β-unsaturated esters and ketones and triphenylbismuth in water and under an air atmosphere [30]. Previous systems utilised for these reactions required strictly anhydrous conditions, thus obtaining high yields in aqueous conditions is a significant step [31]. As before, an oxidative addition step, whereby the Bi–C bond adds across the rhodium centre, was proposed as the first step in the catalytic cycle, with Ph_2BiOH as the bismuth-containing side-product [30]. Miyaura and co-workers reported asymmetric palladium(II) catalysed 1,4-addition reactions of triphenylbismuth to cyclic and acyclic enones, also in aqueous media, with enantiomeric excesses of up to 95% [19]. Further studies include the use of triphenylbismuth in the cross-coupling of aryl bromides and iodides [17,18,20,21,23], acyl chlorides [22,28], vinyl iodides [24], allyl acetates [26] and α-arylacetyl chlorides [25]. Wang and co-workers recently demonstrated the compatibility of bismuth reagents with

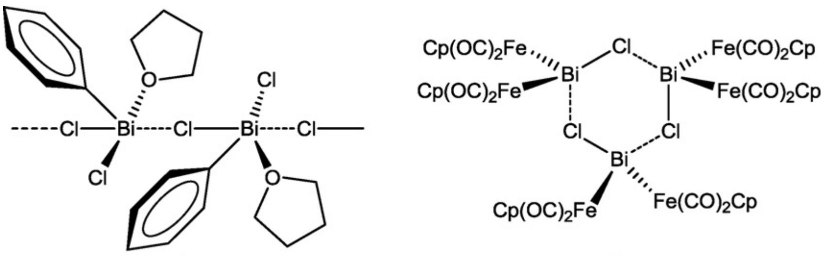
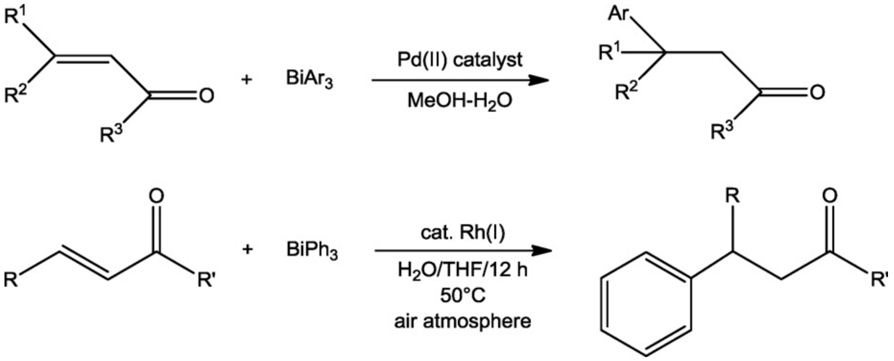
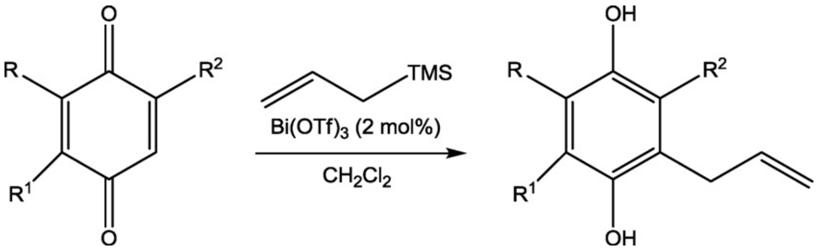


Fig. 1. Examples of oligomeric structures formed by Bi(III) compounds.



Scheme 1. Selected examples of catalysed reactions.



Scheme 2. Bismuth(III) acting as a Lewis-acid catalyst.

the use of a heterogeneous catalytic system [32]. Such generality across a range of substrates makes the study of bismuth reagents, and subsequently their reactivity with low-valent metal centres, an increasingly attractive discipline. A detailed treatment of this topic is beyond the scope of this article; however, such systems have been reviewed recently by Zhang et al. [33] (Scheme 1).

It is worth noting that bismuth species not only have applications as reagents in organic synthesis, but can also be employed as the catalysts themselves (for reviews see references [34–36]). The use of bismuth(III) triflate as a Lewis-acid catalyst to promote nucleophilic addition [37,38], cyclisation [39], Friedel–Crafts [40,41], rearrangement [42] and oxidation [43] reactions is well known (Scheme 2).

$BiCl_3$ can similarly act as a low-cost and air-stable Lewis-acid catalyst in hydroamination reactions, a process traditionally catalysed by late transition metal systems [44]. MoO_3/Bi_2O_3 phases have been utilised as heterogeneous catalysts for the oxidation of olefins, e.g. the allylic oxidation of propene, exhibiting good selectivity and focussing research into the synthesis of molecular molybdenum-bismuth species [45]. $BiPh_3$ has demonstrated the ability to mediate the Lewis acidity of $TiCl_4$ by the formation of a Lewis-acid-base adduct, which can be used as a catalyst in selective Diels–Alder cycloadditions [46]. Rhenium–bismuth nanoparticles have also been shown to act as effective catalysts under mild conditions in the synthesis of a vitamin B_3 precursor, nicotinonitrile [47].

Pentacarbonyl chromium derivatives of Bi have also been shown to facilitate the activation of MeOH via the cleavage of the C–O bond (Scheme 3) [48]. Such applications make the synthesis of metallated complexes of Bi desirable in contemporary chemistry.

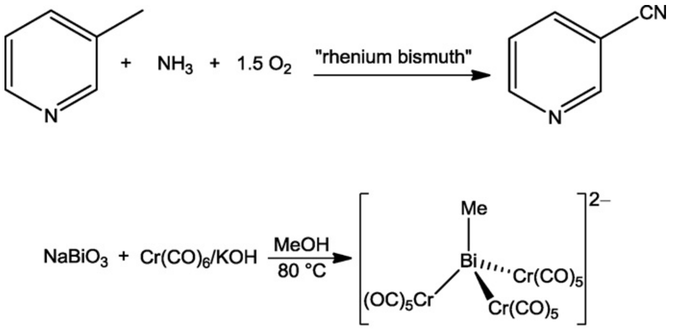
This review aims to demonstrate the multi-faceted nature of the transition metal chemistry of bismuth and provide a detailed coverage of this topic. Several excellent reviews have been published that cover some of the aspects presented here, notably those of Whitmire and Norman on clusters [49–51], Roggan and Limberg on molybdenum-bismuth chemistry [6] and Mehring on the chemistry of the mixed bismuth–transition metal oxides [52]; however, no specific, up to date treatment is currently available.

2. Compounds based on the cyclopentadienylcarbonyl metal fragment

2.1. Synthesis and reactivity of iron-containing species

Consisting, in general, of a central Bi atom connected to up to three 17-electron cyclopentadienylcarbonyl iron fragments, this class of compounds, as exemplified in Fig. 3, was first reported in 1971 by Cullen et al., who synthesised a series of molecules containing E–Fe σ-bonds (E = As, Sb and Bi) [53,5].

The relevant species described is $[\{Cp(CO)_2Fe\}BiCl_2]$ (X = Cl: **4**), ($Cp = \eta^5\text{-}C_5H_5$). In this first instance, the above compound was derived from the reaction of the dimeric $[Cp(CO)_2Fe]_2$ with $BiCl_3$ in dichloromethane, which resulted in the formation of the chlorinated iron side-product $[Cp(CO)_2FeCl]$. In a further study conducted by the same group, the mechanism of the reaction was probed and an insertion reaction postulated, whereby the $BiCl_3$ first inserts into the Fe–Fe bond, yielding a Bi^V intermediate. A second step results in the elimination of the side-product, and so is consistent with experimental evidence; however, an ionic mechanism is also possible. In a later study, the crystal structure of the analogous, but more kinetically stable, compound $[\{Cp''(CO)_2Fe\}BiCl_2]$ ($Cp'' = 1,3$-



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Scheme 3. Examples of use of transition metal–bismuth compounds in synthesis.

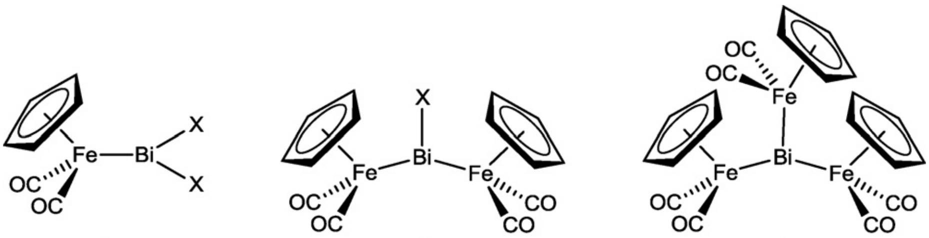

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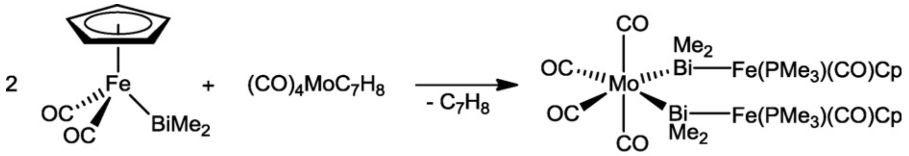
Fig. 3. General set of structures showing the mono-, bi- and trimetallated species.



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Scheme 4. Synthesis of $[Cp(CO)(Me_3P)Fe(BiMe_2)]_2Mo(CO)_4$ (**7**).

$C_5H_3tBu_2$) was obtained [54]. The compound was shown to adopt a polymeric structure in the solid state, through the presence of intermolecular Cl–Bi···Cl interactions, consistent with the known Lewis acidity of Bi^{III}. These short, secondary interactions are 2.971 and 3.245 Å in length. The larger Cp″ ligand serves as a greater steric block, protecting the Bi centre from nucleophilic attack.

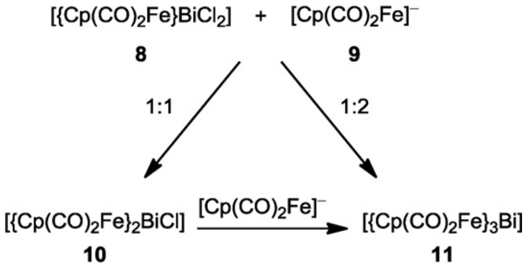
Malisch and co-workers reported the synthesis of the bis(amino)bismuth derivative $[\{Cp(CO)_2\}FeBi(N\text{-}tBu)_2SiMe_2]$ by salt elimination reaction of the chlorinated amino bismuth with the appropriate sodium metallate [55]. Similar structures were reported by Wieber et al., who prepared $[\{Cp(CO)_2Fe\}Bi(SCSOMe)_2]$ and $[\{Cp(CO)_2Fe\}Bi(S_2CNEt_2)_2]$, the latter containing two four-membered rings based around the bismuth atom [56]. Mono-iron species have also been reported for the dibromo-, diiodo-, and dimethylbismuth analogues [5,53,56]. The related trimetal species $[Cp(CO)(Me_3P)Fe(BiMe_2)]_2Mo(CO)_4$ was prepared by Malisch in 1983, by the reaction of $[\{Cp(CO)(PMe_3)Fe\}BiMe_2]$ with the norbornadiene molybdenum carbonyl complex (Scheme 4) [57]. The metal fragment is able to *cis*-coordinate two of the substituted bismuthanes, resulting in an optically inactive, 1:1 mixture of diastereoisomers. No interconversion between geometrical isomers was observed, even in boiling benzene.

The bismuth centre can also act as a bridging ligand between such organoiron fragments, and the compounds $[\{Cp(CO)_2Fe\}_2BiCl]$ (**10**) and $[\{Cp(CO)_2Fe\}_3Bi]$ (**11**) have also been extensively studied [13,58]. Various synthetic routes to such compounds have been applied, including the reaction of the above dichloro species with activated magnesium [54] and the low or room temperature reaction of $BiCl_3$ with $Na[Cp(CO)_2Fe]$ in the appropriate stoichiometries [13,54]. The syntheses of the above compounds are displayed in Scheme 5. Both the μ_2- and μ_3-bridged species contain unbridged Fe–Bi bonds, with Fe–Bi–Fe bond angles that are close to tetrahedral [13]. These bond angles are large in comparison with other trivalent bismuth species, such as $BiMe_3$, an observation which can be explained in terms of the increased steric bulk of the metal fragments. The μ_2-bridged species adopts a trimeric, six-membered, planar ring structure in the solid state, due to intermolecular interactions analogous to those previously described for the solid state structure of $[\{Cp(CO)_2Fe\}BiCl_2\}]$ (**8**). The geometry about each bismuth centre in the Bi_3Cl_3 ring was described as distorted tetrahedral, the deviations from conventional tetrahedral were reportedly caused by the presence of a stereochemically active lone pair of electrons on each of the bismuth atoms. This lone pair lies in the Fe_2Bi plane of the structure. The μ_3-bridged species is monomeric in nature and adopts a trigonal–pyramidal structure about the central bismuth atom.

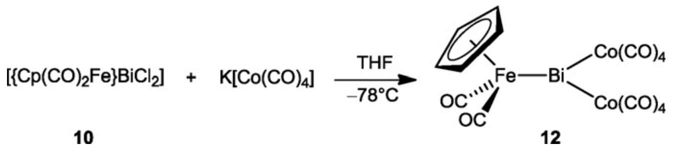
Variation of the bismuth-containing starting material allows wider functionalisation at the bismuth centre. Examples are provided by the studies on transition metal–bismuth nitrates $[(NO_3)Bi(ML_n)_2]$, which can be synthesised by $Bi(NO_3)_3{\cdot}5H_2O$ and the corresponding metallate [59]. The chloride can also be exchanged for a thiocyanate by the use of a source of $Bi(SCN)_3$ as the starting material [60].

The reactivity of the aforementioned cyclopentadienylcarbonyl iron-bismuth species has been extensively studied and many products have been fully characterised. As shown in Scheme 5, $[\{Cp(CO)_2Fe\}BiCl_2]$ (**8**) reacts with activated magnesium to give the anionic species $[Cp(CO)_2Fe]^-$, $MgCl_2$ and elemental Bi. A further equivalent of $[\{Cp(CO)_2Fe\}BiCl_2]$ (**8**) can then react with the nucleophilic species to yield the bridged species described above. The compound can also react with other nucleophiles, such as $K[Co(CO)_4]$, which yields the heterosubstituted bismuthane $[\{Cp(CO)_2Fe\}\{\mu_3\text{-}Bi\}\{Co(CO)_4\}_2]$ (**12**) in a substitution reaction [61]. $[\{Cp(CO)_2Fe\}_2BiCl]$ undergoes a substitution reaction when treated with triethylaluminium, to give $[\{Cp(CO)_2Fe\}_2BiEt]$ [58] (Schemes 6 and 7).

An equilibrium exists between the two bismuth-bridged species which is of synthetic utility [58]. The μ_2-species can react with one equivalent of the $[Cp(CO)_2Fe]^-$ anion to yield the μ_3-bridged species. If an equivalent of BiX_3 (X = Cl, Br, I) is added to the reaction mixture, the μ_2-species is regenerated, meaning that each can be used as a precursor for the formation of the other. These redis-



Scheme 5. Reaction of $[\{Cp(CO)_2Fe\}BiCl_2]$ (**8**) with activated magnesium to generate $[\{Cp(CO)_2Fe\}_2BiCl]$ (**10**) and $[\{Cp(CO)_2Fe\}_3Bi]$ (**11**).



Scheme 6. Synthesis of **12**.

$$\underset{\mathbf{13}}{2\,\mathrm{Na[Fe(CO)_2Cp]}} + \mathrm{BiCl_3} \longrightarrow \underset{\mathbf{14}}{1/3\,[(\{\mathrm{Fe(CO)_2Cp}\}_2\mathrm{BiCl})_3]} + 2\,\mathrm{NaCl}$$

$$\underset{\mathbf{13}}{3\,\mathrm{Na[Fe(CO)_2Cp]}} + \mathrm{BiCl_3} \longrightarrow \underset{\mathbf{15}}{[\mathrm{Bi\{Fe(CO)_2Cp\}_3}]} + 3\,\mathrm{NaCl}$$

Scheme 7. Synthesis of the cyclopentadienylcarbonyl compounds **14** and **15** by salt elimination reactions.

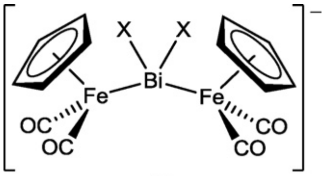


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Fig. 4. General four-coordinate anion (**16**) generated by the addition of X^- to the bimetallic species.

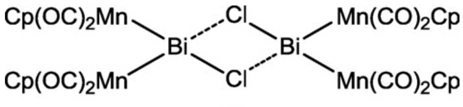

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Fig. 5. Solid state structure of [$\{\mathrm{Cp(CO)_2Mn}\}_2\mathrm{BiCl}$] (**19**), which crystallises as a dimer.

tributions are evident in the mechanisms for the salt elimination reactions that yield the bridged compounds.

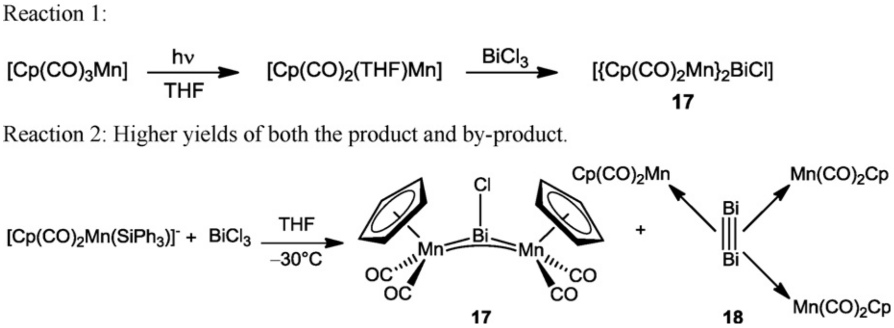
The μ_2-bridged species also reacts with sources of chloride, to give four coordinate, anionic bismuth species which can be crystallised as salts [62,63]. For example, [$\{\mathrm{Cp(CO)_2Fe}\}_2\mathrm{BiCl}$] reacts with equimolar quantities of [$\mathrm{N(PPh_3)_2}$]Cl to give the ionic complex [$\mathrm{N(PPh_3)_2}$][$\{\mathrm{Cp(CO)_2Fe}\}_2\mathrm{BiCl_2}$]. Such anions can be isolated for the analogous molybdenum and tungsten compounds, and the analogous bromide chemistry can also be observed. The four-coordinate anions produced contain Bi–Cl bond lengths that are significantly longer than the standard single-bond length, but are comparable with those found in previous structures where secondary Cl–Bi···Cl interactions are present. The geometry about the bismuth centres in such complexes can be described as equatorially vacant trigonal bipyramidal, with the chlorides in axial positions. This distortion from the regular tetrahedral geometry brings about a stabilisation of the $3a_1$ orbital of the bismuth atom, which is the HOMO, and so is favourable over the less sterically strained tetrahedron (Figs. 4 and 5).

A series of isoelectronic four-coordinate cations were also generated by Norman and co-workers, of the general formula [$(\mathrm{Cp(CO)}_x\mathrm{M})_2\mathrm{Bi}\{\mathrm{OP(NMe_2)_3}\}_2$][$\mathrm{PF_6}$] (M = Fe, Mo; x = 2, 3) [64]. The crystal structure of the iron compound revealed an equatorially vacant trigonal bipyramidal geometry at bismuth, with the iron fragments occupying the equatorial positions. Comparison with the aforementioned anionic species reveals that the structures are similar, with slight discrepancies in the bond angles.

2.2. Complexes containing bismuth–manganese bonds

An analogous series of structures exists where the iron fragment is replaced by the corresponding molybdenum, tungsten, chromium and manganese moieties. The bimetallic species can be accessed for all of the aforementioned metals; however, the trimetallic bismuthane is only known for the molybdenum and chromium chemistry. An extensive study into the synthesis and reactivity of the "bismuthinidene" species [$\{\mathrm{Cp(CO)_2Mn}\}_2\mathrm{BiCl}$] (**17**), which is dimeric in the solid state, was published by Von Seyerl and Huttner [65]. Two contrasting synthetic routes were applied, both of which were also applied to the Cp′ (Cp′ = η^5-$\mathrm{C_5H_4Me}$) analogue, the first of which requires the formation of the adduct [$\mathrm{Cp(CO)_2Mn(THF)}$] by the photolysis of [$\mathrm{Cp(CO)_3Mn}$] in THF, before reaction with a THF solution of $\mathrm{BiCl_3}$ [65]. The second synthesis utilises the reaction of the anionic species [$\mathrm{Cp(CO)_2Mn(SiPh_3)}$]$^-$ with one equivalent of $\mathrm{BiCl_3}$ [66,67], which results in a higher yield of the bismuthinidene product but also increased formation of the side-product **18**, a triply bonded $\mathrm{Bi_2}$ species as shown in Scheme 8.

The dimeric solid state structure of [$\{\mathrm{Cp(CO)_2Mn}\}_2\mathrm{BiCl}$] (**17**) is displayed in Scheme 8, and forms via the secondary Cl–Bi···Cl interactions that were evident for the previously described iron analogues [13]. The Cp′ derivative is essentially monomeric, although the molecules weakly associate to form an infinite spiral chain structure [65]. The dimanganese species has been used to demonstrate the differing reactivity of the so called "bismuthinidenes" with other main group "inidine" compounds, such as those of arsenic and antimony [68]. In the latter examples, the inidene species acts as a Lewis acid towards phosphines, forming stable, isolable adducts [69]. However, no such adducts form for [$\{\mathrm{Cp'(CO)_2Mn}\}_2\mathrm{BiCl}$] unless the Lewis base is a chelating ligand, as displayed in Fig. 6 [65]. In general, the chelating Lewis base AB substitutes for the chloride, giving a four-coordinate bismuth atom, the geometry about which can be described as pseudo-trigonal bipyramidal. This is in contrast to lighter group 15 analogues which adopt tetrahedral geometries about the central atom [70]. Such $\mathrm{Bi^I}$ chelate complexes demonstrate some interesting bonding situations. For example, the bonding present in the mixed oxygen and nitrogen donor ligand can be compared with that of the bismuthinidene



Scheme 8. Syntheses of manganese-containing bismuthinidine species, as reported by Huttner et al.

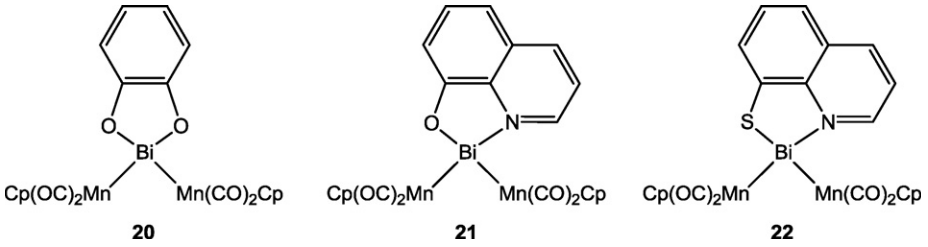


Fig. 6. Series of Bi chelate complexes described by Huttner et al.

species. The relatively short Bi–N bond (2.46 Å), and so the interaction between the N and Bi fragment can be considered a N–σ-donor Bi–π-acceptor interaction, whereas in the bismuthinidene species the Bi-acceptor p-orbital is used in a three-centre, four-electron bond by interacting with the Mn d-orbitals. This results in a lengthening of the Bi–Mn bonds in the chelating complex with respect to the starting material. Such observations allowed the identification and trapping of a bismuth cumulene cation, featuring Mn = Bi double bonds, with the chelating bipyridine ligand.

2.3. Complexes containing bismuth–group 6 metal bonds

2.3.1. Chromium compounds

A limited number of compounds of this type have been synthesised, the earliest of which were reported by Malisch, who prepared $[\{Cp(CO)_3Cr\}_2BiR]$ (R = Me, Br) and $[Cp(CO)_3CrBiMe_2]$ via the reactions of the metal anion in various stoichiometries with Me_2BiBr [71]. Calderazzo et al. utilised the exchange reaction between $[Cp_2(CO)_6Cr_2]$ and Bi_2Ph_4 to prepare $[Cp(CO)_3CrBiPh_2]$ (**23**), which proceeds via a radical mechanism to generate $[Cp(CO)_3Cr]$ *in situ* [72] (Scheme 9). Analogous reactions were observed for both the molybdenum- and tungsten-containing dimers. The bimetallic $[\{Cp(CO)_3Cr\}_2Bi(ONO_2)]$ and $[\{Cp(CO)_3Cr\}_2BiCl]$ have also been reported [60,73]. $[\{Cp(CO)_3Cr\}_3Bi]$ was synthesised by reaction of three equivalents of the metal anion with bismuth trichloride, but can also be obtained via a radical reaction similar to that already mentioned [73]. Bonds between bismuth and chromium are considerably weaker than those formed with the heavier group 6 metals, which results in the trimetallic species being unstable in solution with respect to $[Cp_2(CO)_6Cr_2]$.

2.3.2. Molybdenum compounds

Early research into bismuth–molybdenum species showed that the reaction of $BrBiMe_2$ and the sodium molybdate $Na[Cp(CO)_3Mo]$ did not result in the expected dimethyl derivative but instead in twofold substituted $[\{Cp(CO)_3Mo\}_2BiMe]$ and $[\{Cp(CO)_3Mo\}_2BiBr]$ [71]. Monometallated compounds were realised in later studies by Norman and co-workers who obtained $[\{Cp(CO)_3Mo\}BiCl_2]$ via a redistribution reaction, following the treatment of $[\{Cp(CO)_3Mo\}_2BiCl]$ with one equivalent of $BiCl_3$ [74]. The same group reported the synthesis of $[\{Cp(CO)_3Mo\}BiBrPh]$, the solid state structure of which displays secondary Bi···Br interactions approximately *trans* to the Bi–Br bond [75]. Addition of $[Bu_4N]Br$ to this compound yielded the anionic $[Bu_4N][\{Cp(CO)_3Mo\}BiBr_2Ph]$ containing a conventional four-coordinate bismuth atom. Furthermore, the dimeric dication $[\{Cp(CO)_2Mo\}_2Bi_2Cl_6][PPN]_2$ was obtained, which consists of two edge-sharing square-based pyramids about the two bismuth centres, with the four basal positions occupied by chlorides [76].

$$[Cp_2(CO)_6Cr_2] + Bi_2Ph_4 \longrightarrow \underset{\textbf{23}}{[Cp(CO)_3Cr(BiPh_2)]}$$

Scheme 9. Exchange reaction between dimetallic systems.

Both the bimetallic and trimetallic species exist for molybdenum, and are in fact in equilibrium in solution meaning that stoichiometric control is essential for high-yielding synthesis of either target [77–79]. The concentration of $BiCl_3$ is the controllable factor, its addition resulting in redistribution reactions in solution, in accordance with the equilibria. The bimetallic species is of particular interest, as its solid state structure consists of two independent molecules in the asymmetric unit, which have similar conformations but are distinguished by symmetry [74]. The geometry about the bismuth atoms is the usual trigonal pyramidal, with 'piano stool' type geometries about the Mo atoms. One-dimensional polymeric structures are observed in the solid state, held together by Cl–Bi···Cl interactions between neighbouring molecules; however, the interactions only exist between molecules of the same symmetry. This leads to the formation of two, symmetry independent, one-dimensional polymeric chains of the bimetallic species with no inter-chain interactions (**24**) (Fig. 7). The analogous $[\{Cp(CO)_2Mo\}_2Bi(SCN)]$ also crystallises in a polymeric array, in this case supported by intermolecular Bi···NCS–Bi interactions, resulting in a similar four-coordinate disphenoidal geometry about Bi, with the Bi–S and Bi···N interactions at the axial sites [60]. $[\{Cp(CO)_3Mo\}_2Bi(ONO_2)]$ has also been reported, and can be assumed to adopt a polymeric structure in analogy with the corresponding, structurally characterised iron species [59].

In contrast to these polymeric structures, the reaction of $BiCl_3$ with two equivalents of $[Cp(CO)_2Mo(CNtBu)]^-$ resulted in $[\{Cp(CO)_2(CNtBu)Mo\}_2BiCl]$ which is monomeric in the solid state and contains no short range intermolecular interactions between Bi and Cl [74]. Reaction of the pseudohalide-substituted $Bi(SC_6F_5)_3$ with two equivalents of molybdate gives monomeric $[\{Cp(CO)_3Mo\}_2Bi(SC_6F_5)]$, for which the solid state structure was generally similar to that of the chloride analogue, except for the lack of secondary interactions [80]. $[\{Cp(CO)_3Mo\}_3Bi]$ reacts with I_2 in THF to give the bimetallic iodide complex $[\{Cp(CO)_2Mo\}_2BiI]$, which crystallises as a weakly bound dimer [76]. This dimeric structure, and the aforementioned polymeric structure of the Cl derivative, can be disrupted by dissolution in THF, whereby the monomeric THF adduct **25** forms by a strong Bi–O interaction (Fig. 8).

Limberg et al. have reported a series of polymeric $[-O-Bi\cdots O{=}Mo-]_n$ chains, the reactivity of which has also

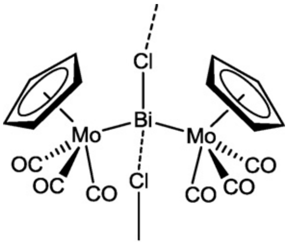


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Fig. 7. One-dimensional polymeric array adopted by $[\{Cp(CO)_3Mo\}_2BiCl]$ (**24**).

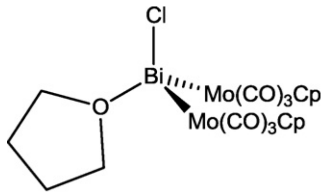

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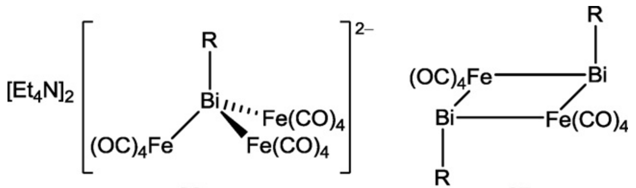
Fig. 8. Disruption of polymeric structure by THF adduct formation.



26 **27**

Fig. 9. Complexes derived from $[Bi\{Fe(CO)_4\}_4][NEt_4]_3$.

been studied [81,82]. The reaction of $[Cp^*(O)_2Mo–O–Bi(o\text{-Tol})_2]_n$ with molybdenocenedihydrides resulted in the elimination of methanol, and the formation of $[^RCp_2(H)MoBi(o\text{-Tol})_2]$ (R = H, Me), which contains a Mo–Bi bond. The authors reported an alternative synthesis of this compound, again using molybdenocenedihydride to disrupt the organobismuth polymer $[MeOBi(o\text{-Tol})_2]_n$ via alcohol elimination. Crystals of $[^{Me}Cp_2(H)MoBi(o\text{-Tol})_2]$ suitable for X-ray diffraction were obtained, the bismuth atom adopts the expected distorted pyramidal geometry, with a Mo–Bi bond length of 2.8976(3) Å that is comparable to those discussed in the previous section.

2.3.3. *Tungsten compounds*

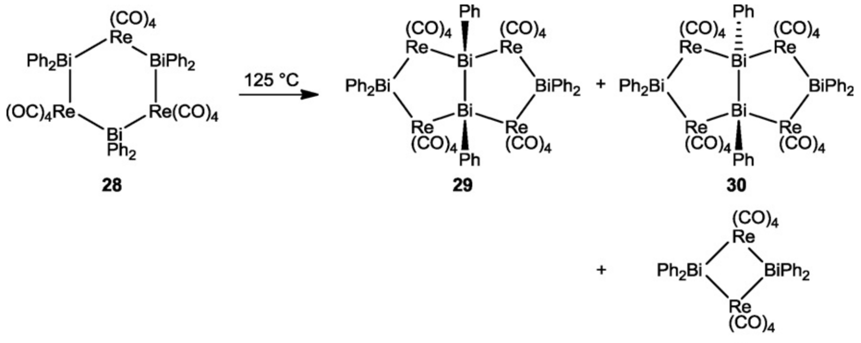
The corresponding tungsten chemistry is largely analogous to that of molybdenum, with mono-, bi- [60,80], and trimetallated species known [6,74]. Panster and Malisch observed the formation of the monometallated $[Cp(CO)_3W]BiMe_2$ from the reaction of $[Cp(CO)_3WH]$ with $BiMe_3$ [71]. This compound displayed reactivity with $[Cr(CO)_5(THF)]$, yielding the interesting four-coordinate bismuth species $[\{Cp(CO)_3W\}BiMe_2\{Cr(CO)_5\}]$. The formation of a coordinate bond between bismuth and chromium is comparable with the behaviour of the trialkylbismuthines, which will be discussed in more detail in a later section. Coordination to chromium brought an end to the observed mobility of the methyl subsituents in the starting material, which resulted in redistribution reactions in favour of $[Cp(CO)_3W]_2BiMe$. The same group also reported the bis(amino)bismuth substituted tungsten fragment $[\{Cp(CO)_3W\}Bi(N\text{-}t\text{Bu}_2)SiMe_2]$, in analogy with the corresponding iron species previously discussed [55]. Another monometallated bismuthine $[\{Cp(CO)_3W\}BiPh_2]$, reported by Calderazzo et al., was shown to react with triphenylphosphine to give the substitution product $[\{Cp(CO)_2(Ph_3P)W\}BiPh_2]$ [72].

3. Compounds based on transition metal carbonyl fragments

Such compounds exist for a wide variety of metals, both molecular structures and larger clusters can be generated, with both charged and neutral species known. These compounds were often synthesised from three-coordinate arylbismuth compounds with metal carbonyls, or alternatively derived from bismuth trihalides. Examples exist in which the starting materials are bismuth oxides, as exemplified by the highly charged cluster anion $[\{(CO)_4Fe\}_4Bi][NEt_4]_3$, which was obtained from the reaction of $NaBiO_3$ with $[Fe(CO)_5]$ in methanol [83–85]. This compound reacts with alkyl halides or dihalides to form $[\{(CO)_4Fe\}_3BiR][NEt_4]_2$ (**26**) or the cyclic compound $[R_2Bi_2Fe_2(CO)_8]$ (**27**) (R = Me, Et, *i*Pr, *n*Bu, *i*Bu, $PhCH_2$, CH_2Cl) (Fig. 9) [86,87]. The cyclic species are favoured upon reaction with highly reactive electrophiles, however, as this reactivity is decreased, the former is increasingly favoured.

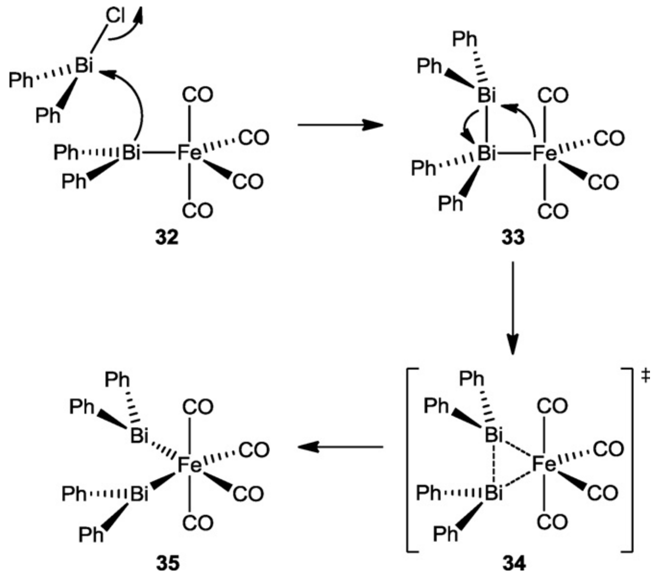
A further unusual complex with a tetrahedral Bi center is the ten-electron $[Cp_2Co][Bi\{Co(CO)_4\}_4]$ reported by Leigh and Whitmire [88]. The bismuth centre has two electrons more than the required eight. A consequence of this hypervalency is the length of the bismuth-cobalt bonds, which range from 2.876 to 2.939 Å, making them significantly longer than those in comparable structures. Metal carbonyl fragments were also used to stabilise the trimeric $[Bi_3]^{3-}$, which is isostructural and isoelectronic with ozone [89]. This resulted in the formation of *closo*-clusters $K(K\text{-crypt})_5[Bi_3Cr_2(CO)_6]\cdot 3en$ and $K(K\text{-crypt})_5[Bi_3Mo_2(CO)_6]\cdot 3en$ (crypt = 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane; en = ethylenediamine). Interestingly, the Bi–Bi = Bi bond angles in both species were very close to 90°, indicating molecular orbitals almost exclusively p in character. The elongation of the Bi–Bi bonds, with respect to the diatomic $[Bi{=}Bi]^{2-}$ and the square $[Bi_4]^{2-}$, reflects the back-donation from the metal fragments into the π^*-orbitals and also the delocalisation of bonding electrons across the entire cluster.

A series of polynuclear species containing rhenium–bismuth bonds were recently reported by Adams and co-workers. The cyclic clusters $[(CO)_8Re_2(\mu\text{-}BiPh_2)]$ (**31**) and $[(CO)_4Re(\mu\text{-}BiPh_2)]_3$ (**28**) were obtained in low yields. Conversion of **31** to **28** and the new cluster $[(CO)_8Re_2(\mu\text{-}BiPh)_2]$ was possible by heating to 110 °C. Futhermore, when **28** was heated to 125 °C it was converted to a mixture of the isomers *cis*- and *trans*-$[(CO)_{16}Re_4(\mu\text{-}BiPh_2)_2(\mu_4\text{-}BiPhBiPh)]$ (**29** and **30**, respectively) and **31** (see Scheme 10) [90].



28 **29** **30** **31**

Scheme 10. Rhenium–bismuth carbonyl clusters.



Scheme 11. Mechanism of formation of $[(CO)_4Fe(BiPh_2)_2]$ (**35**) displaying availability of bismuth lone pair in such a system.

3.1. *Reactions of three-coordinate haloarylbismuth compounds*

Reactions between metal anions and haloarylbismuthines result in covalent bonded bismuth–transition metal compounds, whereby the bismuth retains two organic substituents [91]. An example of such a compound is $[(CO)_5Mn(BiPh_2)]$ which was synthesised by Cassidy and Whitmire using $BiPh_2X$ (X = Cl, I) as the starting material. The diarylhalobismuthines undergo salt elimination reactions upon treatment with $Na[Mn(CO)_5]$ to yield the product. The lone pair on bismuth is retained; however, it has been shown to be "inert" in nature, the lack of hybridisation between the 6s and 6p orbitals resulting in C–Bi–C bond angles very close to 90°. In contrast, the analogous iron-containing species $[(CO)_4Fe(BiPh_2)]^-$ acts as a nucleophile towards further equivalents of $BiPh_2Cl$ yielding $[(CO)_4Fe(BiPh_2)_2]$ (**35**) [92]. $[(CO)_5Re(BiPh_2)]$ was also reported, however, no structural data is available for this compound [93]. When $BiPh_2Cl$ reacts with $[M_2(CO)_{10}]^{2-}$ (M = Cr, Mo and W), four coordinate, anionic species are generated containing two metal fragments, $[\{(CO)_5M\}_2BiPh_2]^-$, one of which is bound by the lone pair. Analogous reactivity was also reported for $[Fe_2(CO)_8]^{2-}$ with $BiPh_2Cl$. The mixed-metal compound $[Ph_2Bi\{Cr(CO)_5\}\{Fe(CO)_4\}]$ was prepared from the reaction of $[(CO)_4Fe(BiPh_2)][PPN]$ with $[(CO)_5Cr(THF)]$ [92]. Following consideration of the bond lengths and angles in the aforementioned compounds, the authors proposed a degree of sp^3-hybridisation of the four-coordinate bismuth species. Such structures provide evidence that the basicity and nucleophilicity of the lone pair is flexible, and depends on whether it is energetically favourable for it to be utilised in bonding (Scheme 11).

Dihaloaryl compounds can also be used as starting materials. The treatment of $PhBiBr_2$ with two equivalents of $K[Co(CO)_3(PPh_3)]$ gives the bimetallated bismuth species $[\{(PPh_3)(CO)_3Co\}_2BiPh]$ in good yields [94].

3.2. *Species synthesised from BiX_3 (X = Cl, Br, I)*

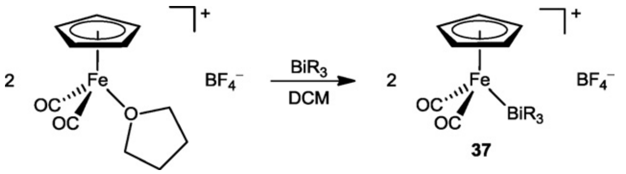
The bismuth trihalides can also be used as precursors for generating bismuth–metal carbonyl compounds, through their reactions with metal carbonyl anions [6,7]. The heteronuclear carbonyl compound $[\{Co(CO)_4\}_4Bi]^-$ was obtained by the reaction of $BiCl_3$ and $Na[Co(CO)_4]$ in a 1:4 ratio in tetrahydrofuran. An alternative synthesis of the same complex was also reported, utilizing an equimolar reaction of $[\{Co(CO)_4\}_3Bi]$ and $Na[Co(CO)_4]$ [95]. Schmid and co-workers reported the synthesis of $[\{Co(CO)_4\}_3Bi]$ by reaction of $BiCl_3$ with the metal anion in a 1:3 ratio. Substitution reactions were also reported, yielding the derivatives $[\{(PPh_3)(CO)_3Co\}_3Bi]$, $[\{(AsPh_3)(CO)_3Co\}_3Bi]$ and $[\{(CO)_4Co\}Bi\{Co(SbPh_3)(CO)_3\}_2]$ [96]. A similar structure was obtained from the reaction of $Bi(NO_3)_3{\cdot}5H_2O$ with $K[Co\{P(OPh)_3\}(CO)_3]$ in tetrahydrofuran, which gave $[Bi\{Co(CO)_3\{P(OPh)_3\}\}_3]$ in a 40% yield [60].

In similar substitution reactions as were described in section 2 for the synthesis of cyclopentadienyl metal–bismuth compounds, $[\{(CO)_5M\}_3Bi]$ and $[\{(CO)_5M\}_2BiX]$ (M = Mn, Re and X = Cl, Br and I) have been synthesised as well as the tetracarbonylchromium analogues [97–99]. The geometry about the bismuth centre can be described as trigonal pyramidal and the complexes form oligomers in solution due to secondary $X\cdots Bi–X$ interactions between neighbouring molecules. As was described in an earlier example, these oligomeric networks are disrupted in THF solution by adduct formation. Cullen et al. prepared a series of iron and cobalt compounds by reaction of appropriate metal anions with $BiCl_3$; $[Bi\{Co(CO)_3PPh_3\}_3]$, $[(Cl_2Bi)Fe(CO)_2(NO)PPh_3]$, $[Bi\{Fe(CO)_2(NO)PPh_3\}_3]$ and $[Bi\{Fe(CO)_3(NO)\}_3]$ were reported therein [5]. The reaction of $BiCl_3$ with three equivalents of the anionic hydride $[PPN][HFe(CO)_4]$ results in the four-coordinate dianion $[PPN]_2[ClBi\{Fe(CO)_4\}_3]$, isolated as black microcrystals from a THF solution [100].

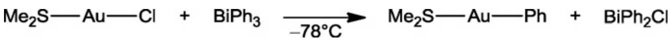
4. The transition metal chemistry of bismuthine ligands

Despite the pronounced Lewis acidity of the majority of bismuth(III) compounds and subsequent weak donor ability of the bismuth lone pair, a series of structures containing bismuthine ligands is reported in the literature, in analogy with the lighter group 15 homologues. The chemistry of the bismuthine ligands bears a greater resemblance to that of the analogous stibines than with the much more basic phosphines, and indeed, review articles have been written which consider stibine and bismuthine ligands together [101,102]. Early examples include the work of Schumann and Breunig, who utilized tris(trimethylgermyl)- and tris(trimethylstannyl)bismuthine to produce a range of compounds of formula $[(CO)_5MBi\{E(CH_3)_3\}_3]$ (M = Cr, V, Mo, W) (E = C, Ge, Sn) [103]. In the same year, McAuliffe and co-workers prepared $[Ni\{Bi(o\text{-}C_6H_4AsMe_2)_3\}X][BPh_4]$ (X = halide), whereby the quadridentate bismuthine ligand coordinates to the nickel(II) centre to give a square-based pyramidal geometry [104]. A series of pentacarbonyl chromium compounds with formula $[(CO)_5CrBiR_3]$ ($R = CH_3$, C_2H_5, C_6H_{11}) were reported by Fischer and Richter as part of a study of the relative basicity of the group 15 "ine" ligands [105]. The triphenylbismuthine analogue was prepared by Carty et al. in a similar study [106]. Talay and Rehder reported the synthesis of $[NEt_4][(CO)_5V(BiEt_3)]$, $[Cp(CO)_3V(BiEt_3)]$ and *cis*-$[Cp(CO)_2V(BiEt_3)_2]$ by the photolysis of the corresponding metal fragment in the presence of $BiEt_3$ [107].

An NMR study of mixed rhodium(II) carboxylate adducts of the form $[\{(CH_3O)_3P\}Rh(O_2CR)_4L]$ (L = donor ligand), prepared in solution, allowed the construction of the following sequence of decreasing *trans*-influence: $-P(OCH_3)_3 > P(OPh)_3 \approx PPh_3 > AsPh_3 > SbPh_3 \approx py > NH(C_2H_5)_2 > N(C_2H_5)_3 > C_6H_5NH_2 > NCO^- > CH_3CN \approx PhCN > CH_3NCS > PhNCS > BiPh_3 > H_2O \approx (CH_3)_2CO \approx THF$ [108,109]. The triphenylbismuthine ligand exerts a relatively weak *trans*-influence compared with its lighter homologues of phosphorus, arsenic and antimony, reflecting the reduction in donor strength upon descending the group. The effect, on the catalytic activity of $[RuH(COD)(PMe_2Ph)_3][PF_6]$ towards the hydrogenation



Scheme 12. Synthesis of $[FpBiR_3][BF_4]$ (R = Et, Ph).



Scheme 13. Example of a reaction carried out in an attempt to observe a dative interaction between bismuth and gold.

of 1-heptyne, of the addition of group 15 donor ligands to the system was also studied [110]. The system containing $BiPh_3$ showed a lower catalytic activity than the corresponding phosphine- and stibine-containing systems, however, it displayed a greater activity than that of the corresponding arsine.

Whereas the number of structures containing stibine ligands increased significantly in the following decade, only a small number of bismuthine–transition metal compounds were reported [111]. A series of seven-coordinate molybdenum and tungsten complexes were synthesised by Baker and Fraser, the compounds $[I_2(CO)_3M(BiPh_3)_2]$ (M = Mo, W), $[I_2(CO)_3(NCMe)M(BiPh_3)]$, $[(\mu\text{-}I)I(CO)_3Mo(BiPh_3)]_2$, $[I_2(CO)_3\{P(OPh)_3\}M(BiPh_3)]$, $[I_2(CO)_3(AsPh_3)Mo(BiPh_3)]$ and $[I_2(CO)_3(PPh_3)W(BiPh_3)]NCMe$ were reported therein [112]. In a further study, $[I_2(CO)_3(NCMe)Mo(BiPh_3)]$ was shown to react with one equivalent of 2,2′-bipyridyl to give the cationic $[I(CO)_3(bipy)Mo(BiPh_3)]I$ [113]. In 1991, Schumann and Eguren reported the synthesis of the bismuth-containing cationic species $[FpBiR_3][BF_4]$ (**37**) (Fp = $Cp(CO)_2Fe$, R = Et, Ph) by displacement of tetrahydrofuran from $[Fp(THF)][BF_4]$ in dichloromethane [114] (Scheme 12). The crystal structure of the phenyl derivative showed a pseudo-octahedral geometry at iron and an iron-bismuth bond length of 2.570(1) Å, consistent with a largely σ-bonded system.

A similar methodology was employed by Levason, who used the THF adducts of the group 6 metal carbonyls and $BiPh_3$ to prepare $[(CO)_5MBiPh_3]$ (M = Cr, Mo, W), the coordination of $BiPh_3$ to molybdenum carbonyl compounds had previously been reported by Houk and Dobson and also by Schumann [115–119]. The crystal structures of the Mo and W compounds show an octahedral geometry at the metal centre, with $BiPh_3$ occupying an axial position, which is reflected in an increase of the $^1J_{W\text{–}C}$ coupling constant for the *trans* carbonyl. In a later paper, the same group synthesised the previously reported cationic $[FpBiPh_3][BF_4]$ by reaction of $[Fp(THF)][BF_4]$ with $p\text{-}Ph_2BiC_6H_4BiPh_2$, via cleavage of a C–Bi bond [117]. Studies conducted attempting to observe such dative interactions between bismuth and gold, through the reactions of $BiPh_3$ and $BiMePh_2$ with various gold-containing precursors, failed, with the Bi reagent arylating the Au (Scheme 13) [120].

Following a reinvestigation of previous results, Breunig et al. reported the crystal structures of the $Bi(tBu)_3$ analogues of the aforementioned six-coordinate Cr and W pentacarbonyl compounds (Fig. 10) [121]. These structures revealed the bismuth–transition metal dative bond to be slightly longer than those in the corresponding $[(CO)_5MBiPh_3]$ (M = Cr, W). The distorted tetrahedral geometry at bismuth was reported to indicate the adoption of hybrid orbitals with largely p-orbital character. A further compound (**41**) was also reported, whereby the bismuthine ligand coordinates to the cyclopentadienylcarbonyl manganese fragment. This compound exhibits a Bi–Mn dative bond shorter than the usual covalent bond (Fig. 11).

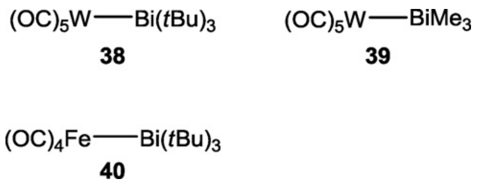


Fig. 10. Transition metal carbonyl bismuthine compounds.

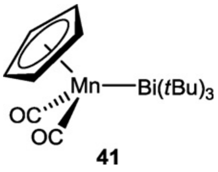


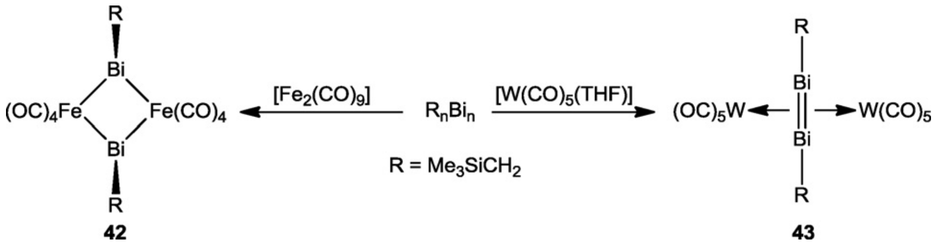
Fig. 11. A cyclopentadienylcarbonylmanganese bismuthine complex.

The same group went on to publish the structures of $[(CO)_5MBiMe_3]$ (M = Cr, W) alongside the stibine analogues [122]. A theoretical investigation of the bonding in such compounds indicated similar ligand properties between the stibines and corresponding bismuthines, with only a slight reduction of donor strength for the latter. The calculations suggested that the bonding can be described using the Dewar–Chatt–Duncanson model [123], with donation being the dominant term. The stibines were shown to be stronger acceptors than the bismuthines. Substitution of the bismuthines with the corresponding stibines showed the stibine compounds are more stable. The trigonal bipyramidal $[(CO)_4FeBi(tBu)_3]$ was also reported, the bismuthine occupying an axial position, with a distorted tetrahedral geometry at bismuth observed.

5. Transition metal compounds of dibismuth

The organometallic chemistry of dibismuth compounds has been largely developed by Breunig et al. and a variety of structures exist whereby dibismuthenes and –ynes coordinate transition metal fragments [124,125]. The inactivity of the bismuth lone pair in such species means that the metals are largely coordinated by the electrons in the double or triple Bi–Bi bond. The reactions of neopentyl- [126] and trimethylsilylmethyl-cyclobismuthanes [127] with the transition metal carbonyl compounds $[Fe_2(CO)_9]$ and $[W(CO)_5(THF)]$ lead to cyclic and side-on coordinated dibismuthane complexes, respectively [128–130]. The resulting iron complexes, $[\{(CO)_4Fe\}_2(\mu\text{-}BiR)_2]$ (R = Me_3SiCH_2) (**42**), consist of two bridging BiR fragments bonded to two 16-electron metal fragments with no Bi–Bi interactions; however, the reaction with the tungsten reagent produces complexes containing Bi═Bi double bonds (**43**). This varying behaviour allows the metal centres in both examples to achieve a favourable six-fold coordination; in the case of the tungsten complex the electron pairs in the double bond are considered as ligands. This compound can undergo loss of one equivalent of $[W(CO)_5]$ to give a monocoordinate dibismuthene species. Reaction of $[W(CO)_5(THF)]$ with Bi_nR_n (R = 2-$(Me_2NCH_2)C_6H_4$) resulted in the formation of $[\{(CO)_5W\}_2BiR]$ rather than the corresponding dibismuthene [131]. The same group also observed that $[\{(CO)_4Fe\}_2(\mu\text{-}BiR)_2]$ could also be obtained by the reaction of $(BiR_2)_2$ with $[Fe_2(CO)_9]$, via the intermediacy and subsequent dimerisation of $[(CO)_4Fe(BiR_2)_2]$ (Scheme 14).

A more sterically encumbered system was used by Power and co-workers to synthesise $[(CO)_4Fe(Bi_2Ar_2')]$ (Ar′ = 2,6-(2,6-$iPr_2\text{-}C_6H_3)_2\text{-}C_6H_3$) and $[(CO)_4Fe(Bi_2Ar^{\#}{}_2)]$ (Ar# = 2,6-(2,4,6-$Me_3\text{-}C_6H_2)_2\text{-}C_6H_3$) [132]. Both compounds exhibit a *trans*-Bi–Bi double bond with the metal fragment coordinated in an η^2-manner. The bismuth–bismuth bond lengths were observed to increase upon coordination to the metal fragment with respect to the free ligand;



Scheme 14. Reactions of cyclobismuthanes with carbonyl transition metal compounds.

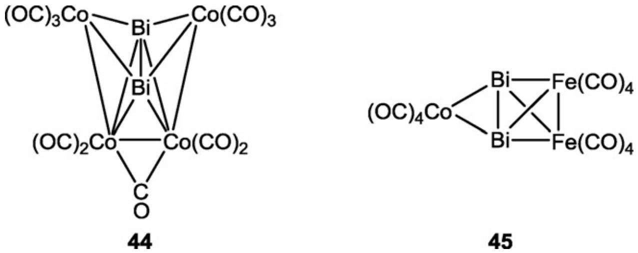


Fig. 12. Dibismuth compounds.

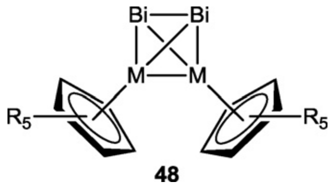


Fig. 13. Structure of $[(\eta^5\text{-}C_5H_4R)_2(CO)_4M_2(\mu\text{-}\eta^2\text{-}Bi_2)]$ (M = Mo, W, R = Me, H) synthesised by Norman et al.

however, at 2.9432(2) and 2.9294(2) Å, they are not long enough to be considered single bonds.

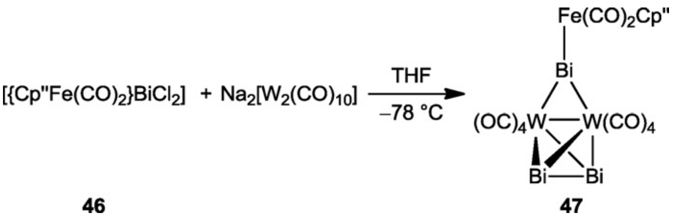
Side-on coordination of a Bi–Bi triple bonds to a transition metal fragment was also observed when $[\{Cp'(CO)_2Mn\}(\mu\text{-}H)]^-$ was treated with $BiCl_3$, yielding the previously mentioned $[\{Cp'(CO)_2Mn\}_3Bi_2]$ [133,134]. An alternative synthesis of this compound was reported by Breunig, via the photolysis of Bi_nR_n ($R = Me_3SiCH_2$) in the presence of $[Cp'(CO)_3Mn]$ [128,129]. The number of such structures was increased in the mid-1980s by variation of the metal carbonyl species and the bismuth starting material. In their efforts to synthesise Zintl-metal carbonylates, Whitmire et al. discovered the varying reactivity of $[(CO)_9Fe_3Bi_2]$ towards $[Fe(CO)_4]^{2-}$ and $[Co(CO)_4]^-$. Whereas the former results in Fe–Fe bond cleavage, the latter leads to Bi–Bi bond formation, yielding $[(Co(CO)_4(\mu\text{-}Bi_2)\{Fe(CO)_4\}_2]$ (Fig. 12) [135].

Depending on the reaction conditions, the reaction of $BiCl_3$ and $[Co(CO)_4]^-$ afforded new clusters, one of which was the monoanionic dibismuth complex $[(CO)_{11}Co_4Bi_2]^-$ (**44**) [136–138].

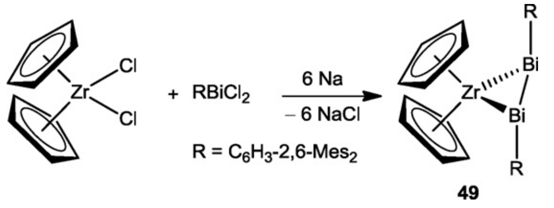
Examples of dibismuth acting as either a four-electron or six-electron donor have been reported in the literature, the latter being the case in the majority of compounds [73]. The tritungsten compound $[\{(CO)_5W\}_3Bi_2]$ [139] and the trimanganese compound described earlier, $[\{Cp(CO)_2Mn\}_3Bi_2]$ [66], contain Bi_2 ligands donating six electrons, which is in contrast to the above ditungsten species. Six and four electron donating species were reported as products of the same reaction, treatment of $(Me_3Si)_2CHBiCl_2$ with $Na_2[W(CO)_5]$ gave $[Bi_2\{W(CO)_5\}_3]$ and $[W_2(CO)_8(\mu\text{-}\eta^2\text{-}Bi_2)(\mu\text{-}BiMeW(CO)_5)]$ [134]. A mixed-metal structure similar to the latter was prepared by Scheer, who obtained $[W_2(CO)_8(\mu\text{-}\eta^2\text{-}Bi_2)(\mu\text{-}BiFe(CO)_2Cp'')]$ from the reaction of $[\{Cp''(CO)_2Fe\}BiCl_2]$ with $Na_2[W_2(CO)_{10}]$ [59] (Scheme 15).

The four-electron-donating dibismuth-containing species $[(\eta^5\text{-}C_5H_4R)_2(CO)_4M_2(\mu\text{-}\eta^2\text{-}Bi_2)]$ (**48**) (M = Mo, W, R = Me, H) were synthesised by Norman et al. by solid state thermolysis or solution-state photolysis of $[\{(\eta^5\text{-}C_5H_4R)(CO)_3M\}_3Bi]$ (Fig. 13) [139]. The dibismuth ligand is twisted with respect to the M–M bond, such that the Bi_2M_2 core displays a tetrahedral geometry in the solid state. This is consistent with the analogous alkyne complex $[Mo_2(CO)_4Cp(\mu\text{-}L)]$ (L = RCCR), the bridging ligand being isolobal with the Bi_2 fragment [134]. A computational study of the Mo compound showed the Bi_2 fragment to have a highest occupied molecular orbital (HOMO) localised between the two Bi atoms; resulting in a strong Bi–Bi σ-interaction and containing little Mo character. The small difference in energy between the Bi_2 π- and highest σ-levels and the Mo frontier orbitals allows interaction, and the Bi_2 σ*-orbital mixes slightly with the high-lying Mo orbitals. Such interactions allow the dibismuth to act as a four electron donor, and the highly localised Bi–Bi σ-interaction allows the possibility of further coordination to an unsaturated metal fragment, giving the commonly observed six-electron donation [139].

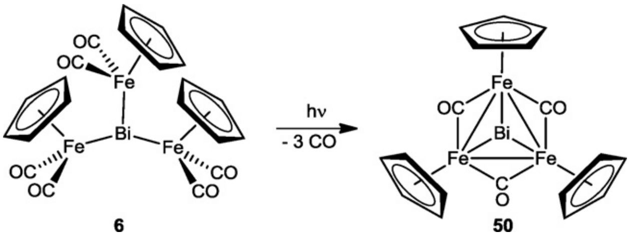
Dibismuthenes can also coordinate to sandwich compounds, as exemplified by the zirconocene derivative $[Cp_2Zr(BiR)_2]$ (**49**) ($R = C_6H_3\text{-}2,6\text{-}Mes_2$) which was synthesised by the reduction of $[Cp_2ZrCl_2]$ with $RBiCl_2$ [8]. The resulting complex is the first example of a $ZrBi_2$ ring, the Bi–Bi bond is lengthened upon coordination to 3.1442(7) Å compared to 2.8327(14) Å in the free dibismuthene RBi = BiR, suggesting a metallacycle rather than a side-on coordination (Scheme 16). A similar structure, the ditungsten complex, $[(CO)_5W(BiR)_2]$ [140], contains a Bi = Bi interaction that is 2.8769(5) Å in length, which is consistent with a π-complex in which two electrons are donated by the Bi = Bi ligand. The zirconocene fragment has 14 electrons whereas the tungsten fragment has 16 electrons. Additionally, the electron releasing nature of the Cp ligands compared to the π-acceptor CO ligands also



Scheme 15. Mixed-metal dibismuth complex.



Scheme 16. Synthesis of side-on coordinated dibismuthene–zirconium sandwich complex **49**.



6 **50**

Scheme 17. Synthesis of [{Cp(μ_2-CO)Fe}$_3$(μ_3-Bi)] (**50**).

plays a part in determining the structures [8]. The significant back-donation into the Bi = Bi π^*-orbital results in the observed bond lengthening, less electron density is available for back-donation from the W fragment.

6. Bismuth-containing clusters

The incorporation of main group elements into transition metal clusters was intensely investigated in the past decades and numerous cluster types were introduced [49,50]. The field of Bi-containing clusters is not clearly defined and we have presented several examples earlier within the related topics. In the following section, we will focus on clusters which contain M–M bonds (M = transition metal) and where the number of transition metals is at least three.

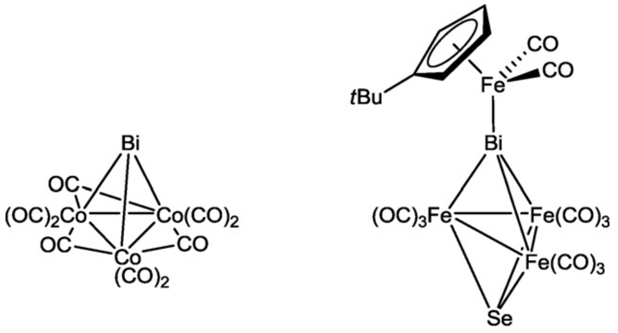
A novel closo-cluster of the first transition series with bismuth was published in 1984 by the research group of Whitmire [84]. They investigated the Lewis basicity of carbonyl oxygen in the presence of bismuth and isolated a related compound [(CO)$_9$Fe$_3$](μ-H)$_3$(μ_3-Bi) [141]. The molecular framework of [{Cp(CO)$_2$Fe}$_3$Bi] allows it to lose three terminal carbonyl groups when exposed to photolysis, to give black crystals of [{Cp(μ_2-CO)Fe}$_3$(μ_3-Bi)] (**50**) as shown in Scheme 17 [13,54]. This compound contains three carbonyl-bridged Fe–Fe bonds, and consists of an Fe$_3$Bi tetrahedral core with an overall symmetry of C$_{3v}$. The Fe–Bi and Fe–Fe bond lengths are comparable to those in systems which have less potential strain [68,84], and the interbond angles are close to the ideal 60° expected for a regular tetrahedron. This formation of a stable *closo*-cluster compound highlights the utility of the bridged species as precursors for further cluster chemistry. As will be discussed in more detail in later sections, the formation of interesting mixed-metal clusters is feasible by this method.

Further examples of bismuth-capped triiron clusters are the anionic cluster [(CO)$_{10}$Fe$_3$(μ_3-Bi)]$^-$ and the first cluster with a Bi/Se combination [Fe$_3${μ_3-BiFe(CO)$_2$(η^5-C$_5$H$_4$*t*Bu)}(μ_3-Se)(CO)$_9$] [142,143]. The following years saw researchers vary the transition metal to produce similar clusters of this structural type. Examples were [(μ_3-Bi)Co$_3$(CO)$_6$(μ-CO)$_3$] [144], [Os$_3$(μ-H)$_3$(CO)$_9$(μ_3-Bi)] and [Ru$_3$(μ-H)$_3$(CO)$_9$(μ_3-Bi)] [145,146] (Fig. 14). The substitution of the latter with monodentate group 15 donor ligands was carried out and the structure of the resulting clusters was proposed [147].

Not only are clusters with one capping bismuth atom known, but also compounds wherein the transition metals are capped on both sides by μ_3-bridging Bi atoms, such as [(CO)$_9$Ru$_3$(μ_3-Bi)] and [(CO)$_{12}$Ru$_4$(μ_4-Bi)$_2$] [148].

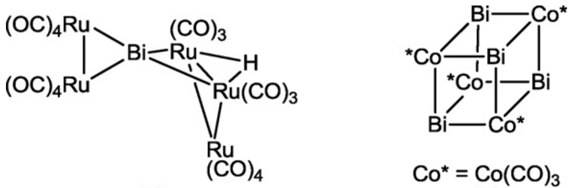
In 1992, the first icosahedral heterobimetallic nickel carbonyl bismuth clusters were reported and the structural features discussed [149]. The drive to synthesise exciting structural types gave rise to a spiro-cluster [{Ru$_2$(CO)$_8$}(μ_4-Bi){(μ-H)Ru$_3$(CO)$_{10}$}] (**53**) [149], cubane-like clusters such as **54** [59,150,151] and large clusters like [PPN]$_2$[Bi$_4$Co$_9$(CO)$_8$(μ-CO)$_8$]·2THF and [PPN]$_2$[Bi$_8$Co$_{14}$(CO)$_{12}$(μ-CO)$_8$]·1.08THF [152] (Fig. 15).

Current research is focused on bismuth-containing subhalides that are on the border between bulk metals and molecular metal cluster compounds [153,154]. Ruck and co-workers reported the rare examples of molecular clusters in the group of bismuth subhalides [{RhBi$_7$}Br$_8$], [Bi$_{10}$Au$_2$](SbBi$_3$Br$_9$)$_2$ and isostructural examples of the latter [155–157].



51 **52**

Fig. 14. Clusters capped by μ_3-bridging Bi atoms.



53 **54**

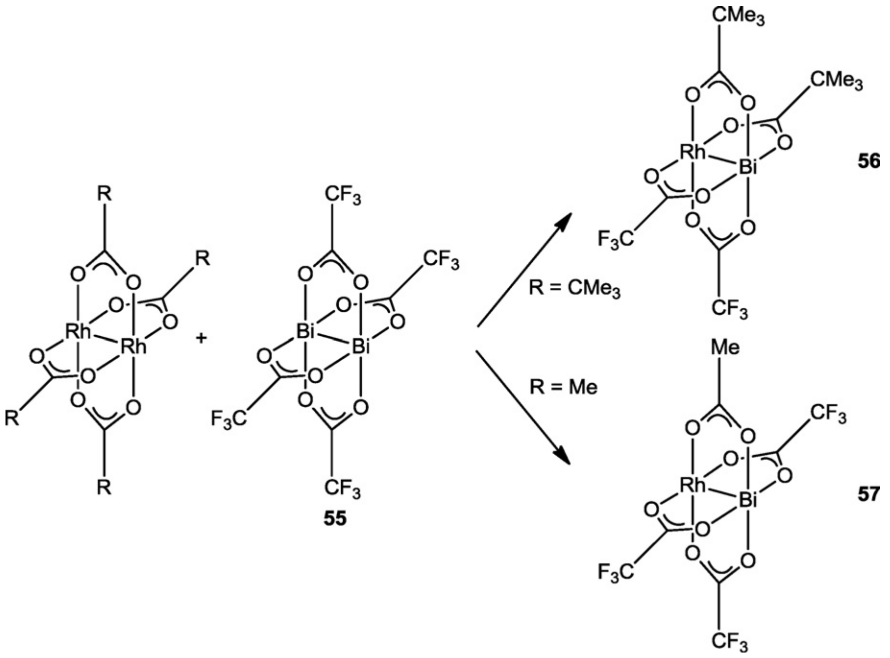
Fig. 15. Spiro and cubane-like clusters.

7. Further complexes and uses in synthesis

7.1. "Paddlewheel" complexes

The catalytic activity of the dirhodium(II,II) "paddlewheel" complex [Rh$_2$(O$_2$CR)$_4$] (R = Me, *t*Bu) towards organic reagents, specifically diazo compounds [158], has led to attempts to incorporate chirality into such structures. A facile solution is the reaction between the aforementioned dirhodium species with the analogous dibismuth trifluoroacetate [Bi$_2$(O$_2$CF$_3$)$_4$] [159], which is able to act as a ligand towards the Rh centre yielding different products depending on the nature of the substituents present in the Rh precursor [160,161]. The first product, obtained when R = *t*Bu, retains two of the carboxylate ligands from the Rh starting material, giving [*cis*-BiRh(O$_2$CF$_3$)$_2$(O$_2$CR)$_2$] (**57**), whereas the second, where R = Me, contains three of the trifluoroacetate ligands (Scheme 18). These products show improved air and moisture stability with respect to the starting materials and are soluble in most common solvents. The molecules crystallise as infinite chains by coordination of a bismuth-bound oxygen to the rhodium centre of the neighbouring molecule. Both complexes were shown to act as Lewis acids towards basic substrates; however, this behaviour was only observed at the Rh terminals of the molecules.

These heterobimetallic paddlewheel complexes form infinite structures when co-sublimed with the aromatic pyrene moiety, whereby aromatic units coordinate at both ends of the molecule [162]. Pyrene coordination is different at either end of the molecule, with an η^2-environment at the Rh end and η^6-coordination at the Bi end, the six Bi···C contacts being in the range 3.359(3) to 3.607(3) Å. This varying coordination results in alternating orientations of the Rh–Bi compound along the chain, with each pyrene coordinated exclusively to two bismuth centres or two rhodium centres. The Bi···C contacts compare favourably with those calculated for the model compound BiMe$_3$·C$_6$H$_6$, in which the bismuth-arene distance is approximately 3.75 Å [163].



Scheme 18. Synthesis of rhodium–bismuth “paddlewheel” complexes.

7.2. Subhalide clusters with rhodium

Ruck and co-workers have published a series of bismuth-containing transition metal subhalide clusters, displaying remarkable structural and bonding features [153,155,164–172]. The rhodium species [{$RhBi_7$}Br_8] was synthesised from its constituent elements in the solid state at high temperature [155]. The bismuth atoms were observed to be arranged in a pentagonal bipyramid about a central rhodium atom. The coordination geometry at bismuth was adjudged to be square-planar with respect to the bromine atoms and a study of the band structure revealed that the axial Rh–Bi bonds are stronger than those in the equatorial plane (Fig. 16).

Xu and Lin studied this compound further, invoking a five-centre, four-electron bonding model to explain the bonding interactions between the equatorial bismuth atoms, observed by Ruck in his calculations [173]. This unusual bonding mode is made possible by the presence of an unused p-orbital on each bismuth atom in the equatorial plane, and accounts for four of the 54 skeletal electrons required for an electron-precise cluster (Fig. 17).

King proposed that the five-centre, four-electron bond could be considered a manifestation of Möbius aromaticity, the first unambiguous case in such a cyclic substructure [174]. The p-orbitals in the Bi_5 plane exhibit σ-type overlap with one phase change, $2k$ molecular orbitals are occupied by $4k$ bonding electrons ($k = 1$), meeting the requirements for Möbius aromaticity. This system can be contrasted with the Hückel aromatic π-system of $C_5H_5^-$, in which overlap occurs perpendicular to the pentagonal plane and no phase changes are present (Fig. 18).

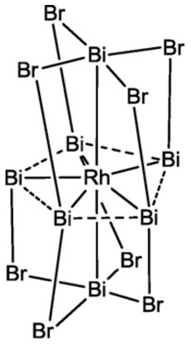


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Fig. 16. Structure of [{$RhBi_7$}Br_8] (**58**) as reported by Ruck.

7.3. “Bent” bismuth–carbon bonds

Another transition metal–bismuth system with interesting properties is that generated by the reaction between [(η^5-C_5H_4R)$_2$$MoH_2$] (R = H, Me) and two equivalents of Bi(O*t*Bu)$_3$ to give [(η^5-C_5H_4R)$_2$MoBi(O*t*Bu)$_2$] (**59**) [175]. When the product is treated with a further equivalent of [(η^5-C_5H_4R)$_2$$MoH_2$], two equivalents of HO*t*Bu are eliminated to give a bismuth-bridged structure [{(η^5-C_5H_4R)$_2$Mo}$_2${μ_2-Bi(O*t*Bu)}$_2$] (**60**) [176]. At room temperature, a further double alcohol elimination occurs, giving two isomeric products (**61**, **62**) containing direct bonds between the bridging bismuth atoms and a carbon atom from the cyclopentadienyl rings, as shown in Scheme 19, hence activating C–H bonds. This elimina-

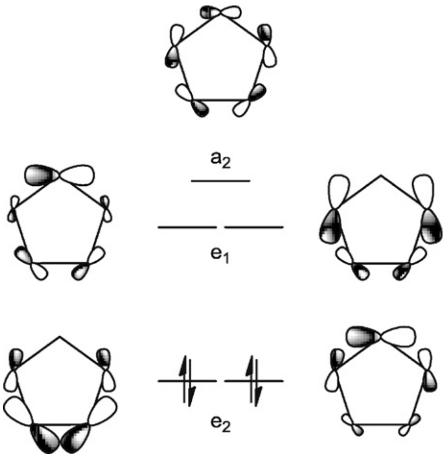


Fig. 17. Orbitals involved in five-centre, four-electron bond as proposed by Lin.

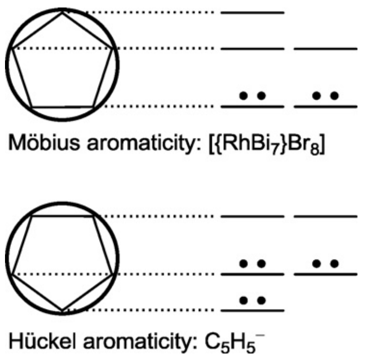
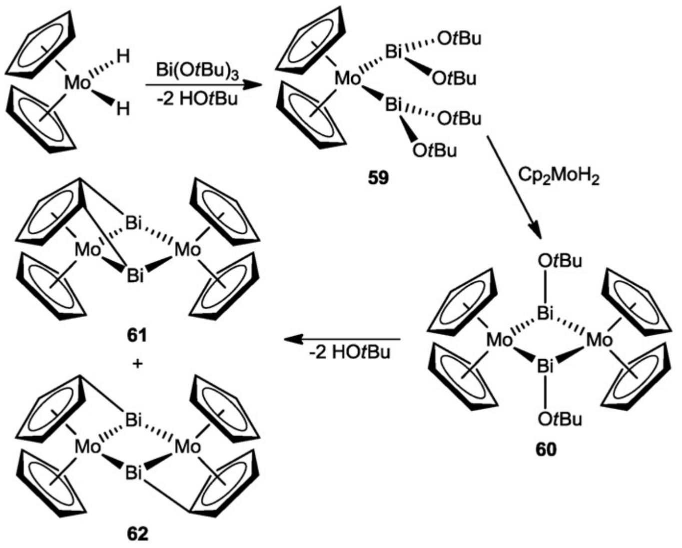
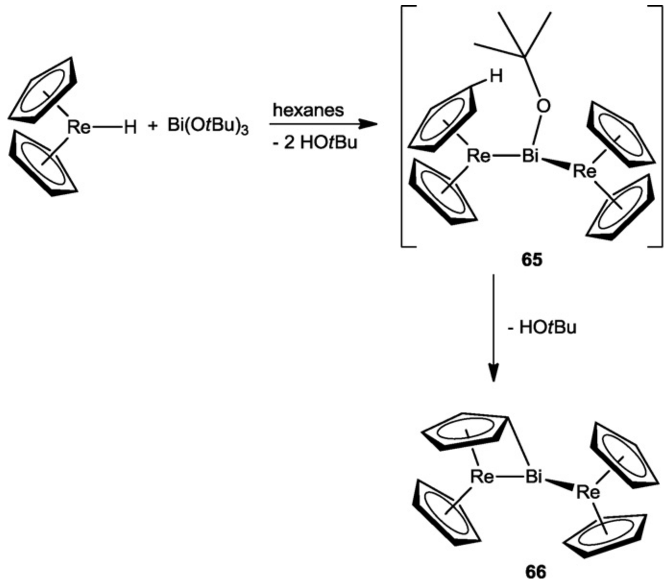


Fig. 18. Comparison of molecular orbitals in Hückel aromatic $C_5H_5^-$ with the Bi_5 planar ring.



Scheme 19. Reactions leading to formation of "bent" Bi–C bonds.



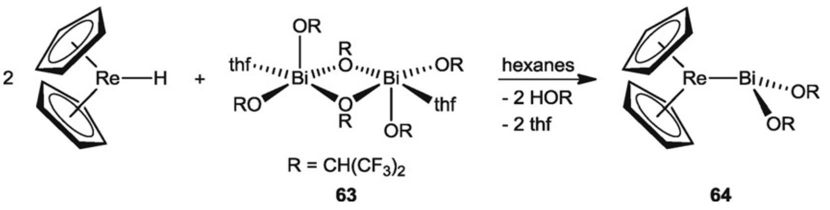
Scheme 21. Reaction sequence resulting in C–H activation in Re system.

tion is facilitated by the close proximity of the cyclopentadienyl H atoms to the alkoxide group, which allows the product with greater thermodynamic stability to form. The Bi–C bonds are surprising in that they are bent out of the plane of the cyclopentadienyl rings by approximately 40°, suggesting a non-linear overlap between Bi and C orbitals. A theoretical investigation into this system showed the two isomeric products to be close in energy, with the unsymmetrical isomer slightly favoured [77]. The calculated Wiberg bond index between the bismuth and carbon centres suggests a relatively strong interaction, with natural bond order analyses indicating 2c–2e bonds polarised towards carbon.

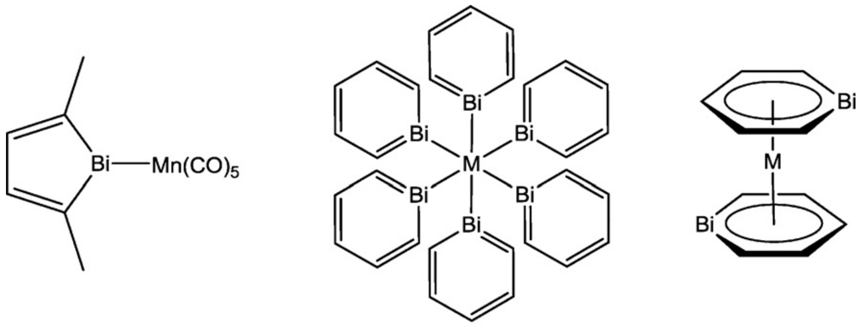
When the analogous reaction was carried out using the bismuth siloxide $Bi(OSiMe_2tBu)_3$, stable derivatives of the bismuth-bridged structures *cis*- and *trans*-$[(Cp_2Mo)_2\{\mu\text{-}Bi(OSiMe_2tBu)\}_2]$ were obtained [177]. No C–H activation was observed by silanol elimination in solution, even over long periods of time. The stability of this system allowed the opening of the aforementioned "bent bonds", by reaction of compound **62** with two equivalents of HOR (R = $SiMe_2tBu$, $SiPh_3$) at room temperature, yielding $[(Cp_2Mo)_2\{\mu\text{-}Bi(OR)\}_2]$, which is observed only as an intermediate for the alkoxide derivative. Such reactivity allows the possibility of extending these systems using metathetical methods, utilising the elimination of R_3SiF.

Limberg and co-workers have recently extended their "hydride-alkoxide" protocol by using rhenocene hydride as the hydride source, generating a "bent bond"-containing structure by alcohol elimination [178]. The initial investigations used $[(MeO)Bi(o\text{-}Tol)_2]_n$ as the alkoxide, low temperature reaction with rhenocene hydride yielded $[Cp_2ReBi(o\text{-}Tol)_2]$, crystals of which were obtained from a hexane solution at 4 °C. At 2.8468(5) Å, the Re–Bi bond is comparable in length to those in the series of Re–Bi carbonyl clusters previously described. The reaction of bismuth trialkoxide $[Bi\{OCH(CF_3)_2\}_3(thf)]_2$ with $[Cp_2ReH]$ in hexane resulted in the isolation of $[Cp_2ReBi\{OCH(CF_3)_2\}_2]$ as an orange powder. The crystal structure revealed a significantly shorter Re–Bi bond length, 2.7032(3) Å, which was interpreted as being indicative of increased polarity of the bond (Scheme 20).

C–H activation, as observed in the above molybdenum system, resulted from the reaction of $[Bi(OtBu)_3]$ with two equivalents of $[Cp_2ReH]$ in hexane. The product, $[CpRe(\mu\text{-}\eta^5,\eta^1\text{-}C_5H_4Bi)ReCp_2]$, forms via the short-lived intermediate $[(Cp_2Re)_2Bi(OtBu)]$, a mechanism which is consistent with observations made by ^1H NMR spectroscopy. Crystals of the product which were suitable for X-ray analysis were obtained, revealing an asymmetric structure whereby the two rhenium–bismuth bonds are of different lengths. The presence of a Bi–C bond of length 2.242(3) Å was also confirmed, which is bent out of the plane by 43.76(12)° (Scheme 21).



Scheme 20. Formation of $[Cp_2ReBi\{OCH(CF_3)_2\}_2]$ (**64**).



67 **68** **69**

Fig. 19. Structures of transition metal–heteroarene complexes (M = Cr, Mo, W).

7.4. Polymerisation of bismuth compounds

Shieh et al. succeeded in obtaining the first example of a continuous ···–Bi–Fe–··· interaction, by way of the polymeric species [*n*BuBiFe$(CO)_4$]$_\infty$, generated by ultrasonification of [{*n*BuBiFe$(CO)_4$}$_2$] [179]. This reaction is thought to proceed via radical cleavage of the Fe–Bi bond in the dimeric species. The crystal structure revealed a 'zig-zag' Bi–Fe–Bi–Fe chain with alternating short and long bismuth-iron bonds (2.771(5) and 2.849(5) Å) and alternating Bi–Fe–Bi and Fe–Bi–Fe bond angles (81.47(12) and 156.46(15)°). The large bond angles at bismuth are surprising given the tendency of bismuth to bond through largely p-hybridized orbitals, in this case, an almost linear Fe–Bi–Fe moiety is observed. Analogous compounds were not obtained when a shorter alkyl chain was present as the substituent on bismuth, indicating that the crystal packing is an important factor in the formation of this species.

7.5. Bismuth-containing heteroarene ligands

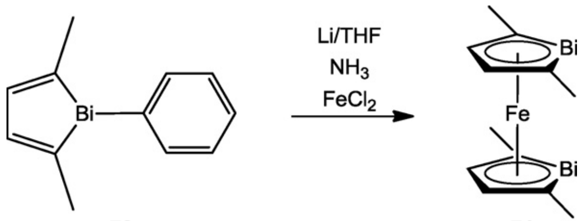
Examples of heteroarene complexes containing bismuth as the heteroatom are known, with both η^1- and η^5-bonding modes for the bismolyl moiety [180]. The reaction of 1-phenyl-2,5-dimethylbismole with lithium at room temperature, followed by the addition of [BrMn$(CO)_5$], produces orange crystals of [(η^1-2,5-dimethylbismolyl)Mn$(CO)_5$] (**67**). Upon heating to the melting point, this compound loses two equivalents of CO to produce the π-complex [(η^5-2,5-dimethylbismolyl)Mn$(CO)_3$]. The η^1-species **67** has a pyramidal geometry about bismuth, and a distorted octahedral geometry about manganese with a Bi–Mn distance of 2.827(1) Å. Spectroscopic data for the η^5-species suggests that the bismolyl ligand is a better π-donor to [Mn$(CO)_3$] than the corresponding group 15 analogues [181,182] (Fig. 19).

A series of heteroferrocenes, in which the bismolyl ligand coordinates to the metal in an η^5 manner, were synthesized by Ashe et al., in order to study the π-bonding between bismuth and carbon [183–186]. The first bismaferrocene to be reported was 2,5-bis(trimethylsilyl)-3,4-dimethyl-1-bismaferrocene, resulting from the sequential treatment of a THF solution of the corresponding bismolyl anion with Li[C_5H_5] and $FeCl_2$ [183]. An X-ray diffraction study showed the central iron atom to be closer to the cyclopentadienyl carbon atoms than to those in the bismolyl ring, and also revealed the displacement of the bismuth atom to a position slightly above the plane of the four carbons. These structural features are attributed to the need of the iron atom to accommodate simultaneous π-bonding with the bismolyl ring carbons and the heteroatom. A less sterically encumbered bismolyl ligand was used to obtain 2,2′,5,5′-tetramethyl-1,1′-dibismaferrocene, containing an iron atom bonded to two eclipsed η^5-bismolyl units (Scheme 22) [184]. A smaller displacement of the bismuth atoms away from the iron (0.28 Å as opposed to 0.39 Å in the previous example), and a Bi···Bi distance of 3.69 Å indicated a secondary inter-ring bonding interaction between the two bismuth atoms. The same methodology was employed to synthesize [$(C_4Me_4Bi)_2Fe$] from the corresponding bismolyl anion [186].

Similar studies were carried out using the heteroarene ligand C_5H_5Bi, which can also bond to metal centres via η^1- or η^6-bonding modes, giving pseudo-octahedral σ-bonded compounds or π-bonded sandwich compounds [187]. Group 6 transition metal compounds [M(η^1-$C_5H_5Bi)_6$] (**68**) and [M(η^6-$C_5H_5Bi)_2$] (M = Cr, Mo, W) (**69**) were analysed using density functional theory calculations (BP86/TZ2P level) and energy decomposition analysis and showed the M–Bi bonding in the η^1 species to be similar in nature to M–CO bonding in the corresponding hexacarbonyl species. The bonding is largely covalent in character with π-interactions of greatest importance, except for the tungsten species where the σ- and π-bonding is of comparable strength. Results for the η^6-species show that the attractive interactions can be accounted for largely by orbital overlap, but approximately 40% is contributed by electrostatics. Comparison with other group 15 analogues showed that the electrostatic contribution is strongest for the bismuth species, leading to stronger bonding between M and C_5H_5E (E = N, P, As, Sb, Bi) for the bismuth derivative. The largest orbital contribution comes from those of δ symmetry, making the bonding similar to that in the bisbenzene analogues.

7.6. Compounds containing group 10-bismuth bonds

Razuvaev and co-workers reported the solid state synthesis of [$(C_6F_5)_2Ge]_3Bi_2$ by the reaction of [$(C_6F_5)_2GeH_2$] with $BiEt_3$ at high temperature [188,189]. Treatment of this ring structure with zerovalent platinum or palladium species [M$(PPh_3)_3$] (M = Pd, Pt) in benzene resulted in the insertion of the transition metal into one of the Ge–Bi bonds. The crystal structure of the product revealed a tricyclic compound, containing non-planar 4-membered (Ge–Bi–Ge–Bi) and five-membered (Ge–M–Bi–Ge–Bi) metallacycles (Fig. 20). The Pt–Bi bond length in **72** is 2.759(3) Å, and the geometry at the platinum-bound bismuth is distorted pyrami-



70 **71**

Scheme 22. Synthesis of bismaferrocenes.

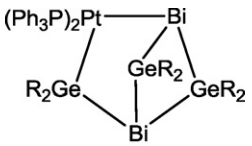


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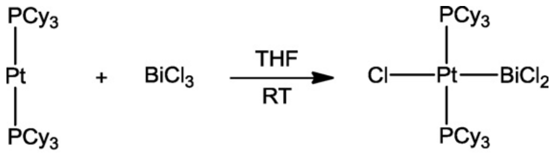
Fig. 20. Polynuclear Ge–Bi–Pt ring (R = C_6F_5).



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Scheme 23. Oxidative addition yielding *trans*-[PtCl(PCy_3)$_2${$BiCl_2$}] (**73**).

dal, with mean Ge–Bi–Pt bond angles of 100.7(1)°. The Ge–Bi–Ge angles in the four-membered-ring are far more acute, at 70.9(2) and 72.2(2)°, than the corresponding angle in the five-membered-ring, which at 87.6(2)° is much closer to the ideal angle of 90°. These distortions from ideal geometries can be attributed to ring restrictions.

The cluster compound [$Bi_4(PdL_2)_4$][Ph_2BiBr_2]$_2$ (L = PPh_2Me) was directly obtained by reaction of PdL_4 and Ph_2BiBr. The first reaction step was anticipated to be an oxidative addition reaction resulting in a cubane-like compound wherein the bismuth atoms define a pseudo-tetrahedron in which the triangular faces are capped by μ_3-PdL_2 fragments [190].

Oxidative addition of the bismuth chloride bond across zerovalent platinum species [Pt(PCy_3)$_2$] was recently observed by our group, resulting in the square-planar platinum(II) compound *trans*-[PtCl(PCy_3)$_2${$BiCl_2$}] (**73**) [191]. The expected distorted pyramidal structure at bismuth was observed, the Cl–Bi–Cl angle (95.63(3)°) indicating significant p-orbital character in the bonding. The Pt–Cl bond distance (2.4155(9) Å) could be used to determine the strength of the *trans*-influence exerted by the –$BiCl_2$ ligand, which was observed to be weak in comparison to those exerted by a series of boryl ligands [192–197] (Scheme 23).

8. Conclusion and outlook

The ability of bismuth species to act as ligands towards transition metal fragments has allowed a wide variety of structures containing transition metal–bismuth bonds to be synthesised. The Lewis acidity of the trivalent bismuth centre often results in oligomeric structures, such as one-dimensional polymeric chains, both in solution and the solid state. This is particularly apparent when halide groups are present allowing X–Bi···X secondary interactions between molecules. Another striking feature is the variation in bonding situations that can be observed when studying the organometallic chemistry of bismuth. For example, dative and covalent interactions have been reported, in addition to cases of dibismuth acting as a two-, four- or six-electron donating ligand.

The focus of this article has been on complexes containing single transition metal–bismuth bonds, largely owing to the existence of very few examples of multiple bonding between the two. The bismuth "cumulene" species [$Cp(CO)_2Mn=Bi=Mn(CO)_2Cp$]$^+$ was proposed as the product of the reaction between [{$Cp'(CO)_2Mn$}$_2$BiCl] and Me_2SiOTf based on spectroscopic evidence and subsequent trapping with bipyridine; however, it was not isolated in crystalline form [66]. A theoretical analysis of M≡Bi bonding (M = Mo, W) revealed such triple bonds to be relatively weak, 64.3 kcal/mol compared to 122 kcal/mol for the phosphorus analogue, and to be largely ionic in character [198].

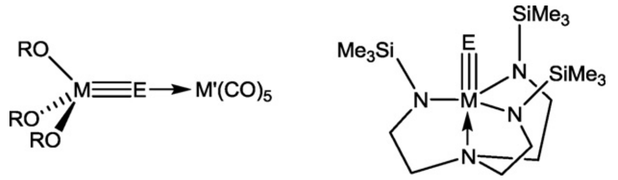

Fig. 21. Structures with kinetically stabilised triple bonds between transition metals and group 15 elements.

Methods used for synthesizing triply bonded systems between transition metals and the other group 15 elements require either coordination of the lone pair centred on the main group atom to a Lewis acidic transition metal fragment or employing bulky organic ligands on the transition metal fragment [1]. This gives the resulting compounds the necessary kinetic stability to be isolated and the possibility of extending this methodology towards a bismuth–transition metal triple bond was discussed by Scheer (Fig. 21). The stabilisation and isolation of transition metal–bismuth multiply bonded systems represents a significant and attractive synthetic challenge for the future.

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